

Two superconducting transition temperatures in LiFeAs detected by ^{75}As nuclear magnetic resonance

S.-H. Baek,^{1,*} L. Harnagea,¹ S. Wurmehl,¹ B. Büchner,^{1,2} and H.-J. Grafe¹

¹*IFW-Dresden, Institute for Solid State Research, PF 270116, 01171 Dresden, Germany*

²*Institut für Festkörperphysik, Technische Universität Dresden, 01062 Dresden, Germany*

(Dated: December 20, 2012)

^{75}As NMR investigation of a single crystal of superconducting LiFeAs is presented. The Knight shift and the *in situ* ac susceptibility measurements as a function of temperature and external field reveal two superconducting (SC) transition temperatures, each of which is associated with its own upper critical field. Strikingly, the Knight shift maintains its normal state value in the SC state at high temperatures, whereas it drops abruptly entering the other state at low temperatures indicating the occurrence of spin-singlet pairing. We discuss that the anomalous SC state at high temperatures emerges due to the extreme sensitivity of the system.

It is commonly argued that superconductivity in iron pnictides is driven by the antiferromagnetic (AFM) spin fluctuations which are associated with nesting between the hole and electron Fermi surface pockets, although the SC gap symmetry seems to vary among the materials from nodal to nodeless [1–3]. An exception in this general picture is LiFeAs that is superconducting as is, without any signature of nesting and static magnetism, yet with rather high $T_c \sim 18$ K [4–6].

While the absence of nesting and static magnetism in LiFeAs [5] might support a non-magnetic origin for the SC pairing, such as phonons [7] or orbital fluctuations [8], AFM spin fluctuations remain a strong candidate that is responsible for the SC pairing [9–12], e.g., by recovering the nesting condition by the magnetic response shifting [13]. If this is indeed the case, it would strengthen the belief that AFM spin fluctuations are fundamental to the superconductivity of iron-pnictides. On the other hand, spin-triplet pairing which is driven by ferromagnetic spin fluctuations originating from strong Hund coupling was also suggested [14], being followed by some experimental supports [15–18]. Such debates about the pairing mechanism in LiFeAs may imply that the nature of superconductivity in this material is different from other iron-pnictide families, and it was suggested that close proximity of the system to a strong magnetic instability may effect the unusual sensitivity of the SC properties [14, 17].

In an effort to confirm the underlying instability and to uncover its nature, we carried out ^{75}As nuclear magnetic resonance (NMR) in a single crystal of LiFeAs chosen from a different batch than those used in our previous NMR study [17], focusing on the low temperature range near and below $T_c \sim 18$ K. Our NMR data clearly show the existence of two SC transition temperatures, one of which is identified by a sharp drop of the Knight shift and the other confirmed by anomalies in both the *in situ* ac susceptibility and the NMR signal intensity. An analysis of the data leads to the conclusion that LiFeAs is indeed very close to a critical instability, which affects

the SC state particularly at high temperatures near the transition temperature.

The single crystal of LiFeAs was grown by a self-flux method as described in Ref. [4]. Due to the sensitivity of the sample to air and moisture, the sample was carefully sealed into a quartz tube filled with Ar gas for NMR measurements. The sealed sample was mounted on a goniometer for an accurate alignment of the sample along the external field. ^{75}As ($I = 3/2$) nuclear magnetic resonance (NMR) experiments were performed in the range of temperature 3.6 — 25 K and external field 0 — 16 T. We also carried out ^{75}As nuclear quadrupole resonance (NQR) to determine the quadrupole frequency ν_Q . The NQR spectrum shows a width of 75 kHz at 20 K, which is much narrower than ~ 170 kHz in a powder sample [19] and thus indicates a sign of good chemical homogeneity of the sample.

The Knight shift \mathcal{K} , i.e., the local static spin susceptibility, was measured from ^{75}As NMR central line at various external fields applied parallel and perpendicular to the crystallographic c axis. The large quadrupole frequency $\nu_Q = 21.08$ MHz of the ^{75}As ($I = 3/2$), which is almost T -independent in the low temperature range investigated, shifts the central transition of the ^{75}As by the second order quadrupole effect given by $\Delta\nu = 3\nu_Q^2/16\omega_n(1 - \cos^2\theta)(1 - 9\cos^2\theta)$ for $I = 3/2$ where ω_n is the unshifted Larmor frequency and θ is the angle between the external field H and the c axis. The Knight shift shown in Fig. 1 was obtained by subtracting $\Delta\nu$ from the total shift of the central line. The SC transition temperature T_c was identified from a sudden drop of \mathcal{K} for a given external field H , which indicates spin singlet Cooper pairing. Whereas this behavior seems consistent with previous other NMR studies in this compound [9, 19], we find that $T_c(H)$, particularly for $H \parallel c$, are much lower than values reported in literature [20–24]. At 8.5 T for $H \parallel c$, for example, \mathcal{K} does not drop down even at 3.6 K, indicating that $T_c \leq 3.5$ K is significantly lower than an expected value (> 10 K) [20–24].

In order to confirm the transition temperature, we

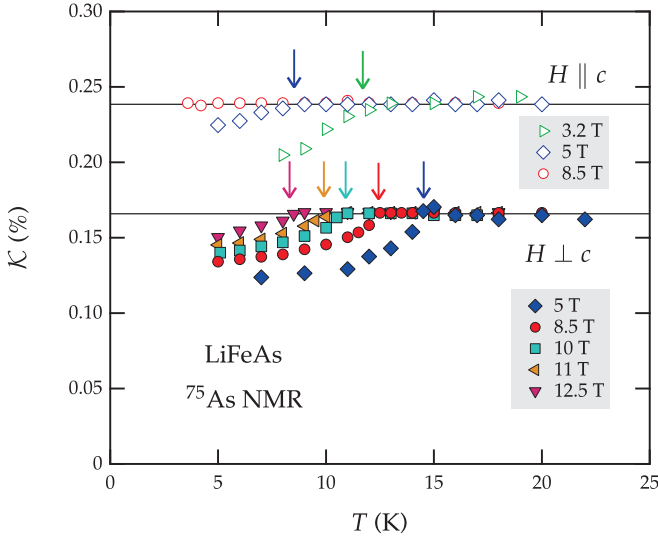


FIG. 1: Knight shift (\mathcal{K}) of ^{75}As as a function of temperature and field for two field orientations. A second order quadrupole correction was made for $H \perp c$. Superconducting transition temperature for each field was determined from the sharp drop of \mathcal{K} as denoted by arrows.

measured the *in situ* ac susceptibility χ_{ac} using the NMR radio frequency (rf) circuit. In the SC state, the Meissner effect induces the change of impedance and thus the tuning frequency of the rf circuit. Therefore, the onset of superconductivity could be detected by monitoring χ_{ac} as a function of temperature. Fig. 2 shows $\chi_{ac}(T)$ measured at various external fields H . Here we define T_c as a temperature where χ_{ac} reaches 10% of the full drop to the low temperature plateau at each field, which are denoted by down arrows. Clearly T_c detected by χ_{ac} is much higher than that obtained by the Knight shift measurements for each field (up arrows). Note that, at 8.5 T parallel to the c axis, a clear onset was observed at 11 K by χ_{ac} which is compatible with values reported thus far [20–24], in stark contrast to the absence of the Knight shift anomaly down to 3.6 K. It may be worthwhile to note that χ_{ac} displays a small but noticeable anomalous change in its slope at T_c obtained by \mathcal{K} .

As the two experimental methods distinguish different onset temperatures of the SC transition, here we define the two transition temperatures obtained by χ_{ac} and \mathcal{K} by T_c^{ac} and T_c^K , respectively. While a sharp drop of \mathcal{K} at T_c^K unambiguously indicates the onset of spin singlet superconductivity, χ_{ac} alone is not sufficient in general to verify whether T_c^{ac} is a bulk SC transition temperature, because other non-superconducting effects might alter the temperature dependence of χ_{ac} . To check the validity of T_c^{ac} , we carefully examined the temperature evolution of the ^{75}As spectra. In the SC state, the signal intensity should decrease due to supercurrents which reduce the sample volume that can be penetrated by the rf field, and therefore it could be another good probe for de-

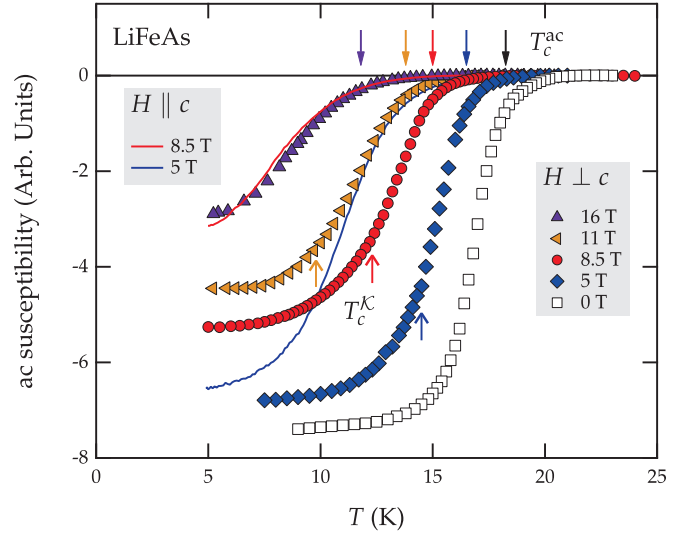


FIG. 2: *In situ* ac susceptibility χ_{ac} measured in the NMR tank circuit as a function of temperature and external field. The transition temperature T_c^{ac} (down arrows) is considerably higher than T_c^K (up arrows) determined by the Knight shift measurements. Data for $H \parallel c$ are shown as solid lines (no arrows for clarity).

tecting the onset of superconductivity. Fig. 3 shows the ^{75}As NMR spectrum as a function of temperature measured at 8.5 T, where the Boltzmann correction was made by multiplying T for each spectrum. For $H \perp c$, the signal intensity starts to decrease at ~ 15 K, which agrees with T_c^{ac} determined from χ_{ac} , as shown in Fig. 3(c). The agreement of the signal intensity with χ_{ac} in their temperature dependences was also confirmed for $H \parallel c$ [see Fig. 3(b) and (c)]. Note that the anisotropy of χ_{ac} below T_c^{ac} remarkably coincides with that of the signal intensity. For direct comparison, \mathcal{K} is shown in the upper panel of Fig. 3(c).

We emphasize that $T_c^{ac}(H)$ indeed confirms bulk superconductivity which has been unanimously proven in our single crystals by numerous other measurements including dc magnetic susceptibility [4], specific heat [25], resistivity [21], angle-resolved photoemission spectroscopy (ARPES) [5, 7, 26], neutron [13], and scanning tunneling spectroscopy (STS) [16], as well as by theoretical supports [27, 28]. Furthermore, $T_c^{ac}(H)$ and the related H_{c2} are in satisfactory agreement with the results measured in other samples by different groups [22–24]. Therefore, we conclude that T_c^{ac} is equivalent to the onset temperature of the *bulk* Meissner effect which modifies the signal intensity and χ_{ac} simultaneously.

Further analysis of the Knight shift, the signal intensity, and the ac susceptibility obtained at various external fields reveals quite different field dependence of T_c^K and T_c^{ac} . (For raw ^{75}As spectra at external fields other than 8.5 T, see supplemental material [29].) The resulting H - T phase diagram is presented in Fig. 4. We find that the

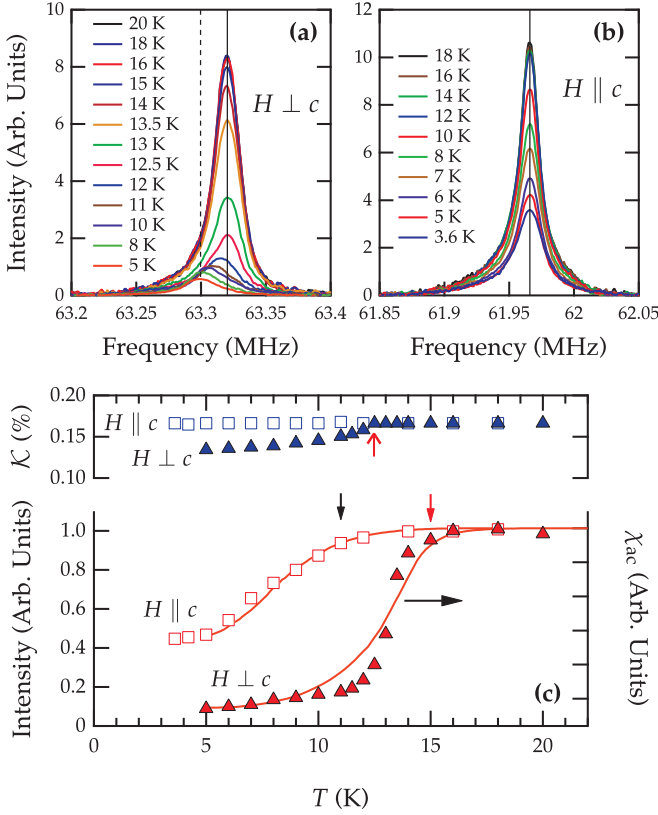


FIG. 3: Temperature dependence of ^{75}As NMR central line at $H = 8.5$ T for (a) $H \perp c$ and (b) $H \parallel c$. (c) Signal intensity and Knight shift versus temperature at 8.5 T. Temperature dependence of signal intensity for both $H \perp c$ and $H \parallel c$ agrees well with that of χ_{ac} , indicating that T_c^{ac} represents the onset of screening due to superconductivity. The Knight shift, however, reveals T_c^{K} which is significantly lower than T_c^{ac} . K_{\parallel} was offset vertically for comparison.

H -dependence of T_c^{ac} is in qualitative agreement with other studies [21, 22, 24]. For example, the data from Khim et al. [24] are compatible with T_c^{ac} data in the H -dependence as well as the anisotropy.

In contrast, the H -dependence of T_c^{K} is very different from that of T_c^{ac} , other than its much lower values. For $H \perp c$, while T_c^{ac} exhibits almost a linear H -dependence up to 16 T, T_c^{K} does not decrease linearly with increasing H . Consequently, the difference $T_c^{\text{ac}} - T_c^{\text{K}}$ becomes larger at higher fields. This trend is more pronounced for $H \parallel c$. Note that the estimated H -dependence of T_c^{K} for $H \parallel c$ (dashed line in Fig. 4) agrees with the absence of T_c^{K} at 8.5 T down to 3.6 K. These observations corroborate that both T_c^{ac} and T_c^{K} represent two SC transitions which take place separately. Further evidence of the two SC transitions is also provided by the specific heat measured in our single crystals. While the Knight shift remains constant down to 3.6 K at 8.5 T (see Fig. 3), specific heat manifests the bulk $T_c \sim 9$ K in a field of 9 T applied along the c axis [25] that is comparable to T_c^{ac} at 8.5 T.

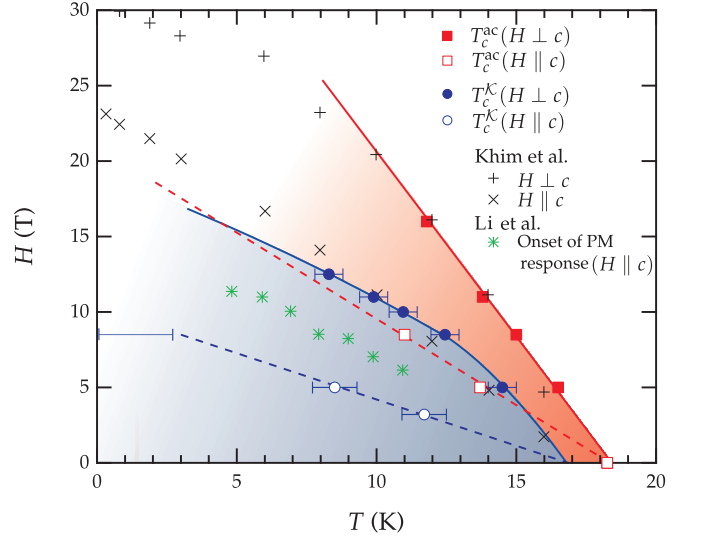


FIG. 4: H - T phase diagram in LiFeAs. Two superconducting transition temperatures T_c^{ac} and T_c^{K} were obtained by the ac susceptibility and the Knight shift, respectively. Data from Khim et al. [24] and Li et al. [18] are shown for comparison. The onset temperatures of the paramagnetic irreversibility from Li et al. are in between T_c^{ac} and T_c^{K} line, while $T_c(H \parallel c)$ in Ref. [18] determined from resistivity (not shown for clarity) almost coincides with $T_c^{\text{ac}}(H)$. Note that shades of blue and red are applicable only to the case of $H \perp c$ and thus some care is needed to compare the data for $H \parallel c$.

Our experimental results naturally raise important questions. Does K , i.e., the intrinsic spin susceptibility, remain unchanged across T_c^{ac} but drop below T_c^{K} ? Do the two SC transitions occur in a single phase? It should be emphasized that only one phase must be present in the normal state above T_c^{ac} , because NMR and NQR spectra exhibit very sharp single lines, and their signal intensities are well conserved at all temperatures investigated. Although inhomogeneous superconductivity is extremely unlikely due to bulk superconductivity in our single crystals, here we discuss the possibility that the two SC transitions result from *phase segregation* in bulk form below T_c^{ac} , i.e., a partial volume fraction of the sample (region I) becomes superconducting at T_c^{ac} first, and the rest of the sample (region II) remains normal down to T_c^{K} but undergoes the SC transition at T_c^{K} .

If phase segregation takes place at T_c^{ac} , the otherwise single spectrum would be segregated into two parts arising from SC region I and normal region II, respectively. In this case, the unchanged Knight shift of the “total” spectrum between T_c^{K} and T_c^{ac} could be realized *only* either (i) if the SC transition in region I is extremely sharp so that the decreasing Knight shift is not detected, or (ii) if triplet superconductivity occurs in region I so that K of region I is still the same as that of the normal region II. The consequence of case (i) should be an almost discontinuous change of the signal intensity just below

T_c^{ac} . On the contrary, we find that the T -dependence of the signal intensity shows a gradual change over a temperature range [see Fig. 3(c)], ruling out this scenario. Similarly, case (ii) is also ruled out as following. Since singlet superconductivity occurs at T_c^{K} , we should have two different SC pairing states below T_c^{K} . Since \mathcal{K} from region II decreases while \mathcal{K} from region I remains constant, two NMR lines or noticeable broadening below T_c^{K} should be observed. As shown in Fig. 3(a), however, the well-defined single line at all temperatures is inconsistent with this scenario. Also by a close inspection of the T -dependence of ^{75}As spectrum at other external fields [29], the phase segregation scenario turns out highly improbable. Hence, we reach a remarkable conclusion not only that \mathcal{K} is indeed a constant in the SC state between T_c^{ac} and T_c^{K} , but also that the two SC transitions take place consecutively in a single phase.

A priori, the unchanged Knight shift through T_c^{ac} contrasts with spin-singlet pairing, because it implies that the spin degree of freedom of electrons does not vanish in the SC state. Surprisingly, another signature of the unusual SC state was also verified by recent magnetometry measurements [18] which report a paramagnetic (PM) response within the SC state at high fields. The onset temperature of PM irreversibility T_{irr} as a function of $H \parallel c$ is located between the T_c^{ac} and T_c^{K} lines (see Fig. 4), whereas T_c determined from resistivity is well consistent with $T_c^{\text{ac}}(H \parallel c)$. The anomalous PM response in the SC state, which is ascribed to the triplet component induced by high fields [18], is indeed in excellent agreement with the nonvanishing spin susceptibility in the SC state revealed by the constant Knight shift. Note that, since T_{irr} is a crossover temperature rather than a measure of the actual transition, $T_{\text{irr}} > T_c^{\text{K}}$ is very reasonable. Therefore, combining our NMR results and Ref. [18], we interpret that both the constant Knight shift and the PM response observed in the similar region of the phase diagram are signs of spin-triplet pairing that could perhaps be stabilized under certain conditions, which may be a realization of the theoretical prediction that a spin-triplet could occur in iron-pnictides depending on various parameters such as Hund coupling and onsite Coulomb repulsion [14, 30, 31].

Interestingly, such a PM irreversibility at high fields was not reproduced in other samples, being attributed to the extreme sensitivity of samples [18] as it was demonstrated in our NMR study [17]. Such a difficult reproducibility of the constant Knight shift behavior as well as of the PM irreversibility suggests that the SC state at high temperatures is unstable in nature, being susceptible to even a tiny off-stoichiometry. We argue that the peculiar sensitivity of LiFeAs is a natural consequence of the close proximity to a critical instability, near which the unusual SC state could emerge. Hence, as long as the off-stoichiometry is small (i.e., the sample quality is pure enough), the effect of the instability would persist

especially at high temperatures/fields causing $T_c(H = 0)$ and $H_{c2}(T = 0)$ very much sample-dependent, whether or not the unusual SC state is actually stabilized. Note that this picture indeed accounts well for the non-trivial large variation of T_c and H_{c2} reported so far in LiFeAs [21–24]. Furthermore, given the possible realization of the anomalous SC state which differs from the usual spin-singlet state, contradicting experimental results regarding the pairing symmetries in LiFeAs [16, 32, 33] may be reconciled with each other, in terms of the closeness to a critical ferromagnetic instability.

This work has been supported by the Deutsche Forschungsgemeinschaft through SPP1458 (Grant No. GR3330/2 and BE1749/13) and through Emmy Noether Programme WU595/3-1.

* sbaek.fu@gmail.com

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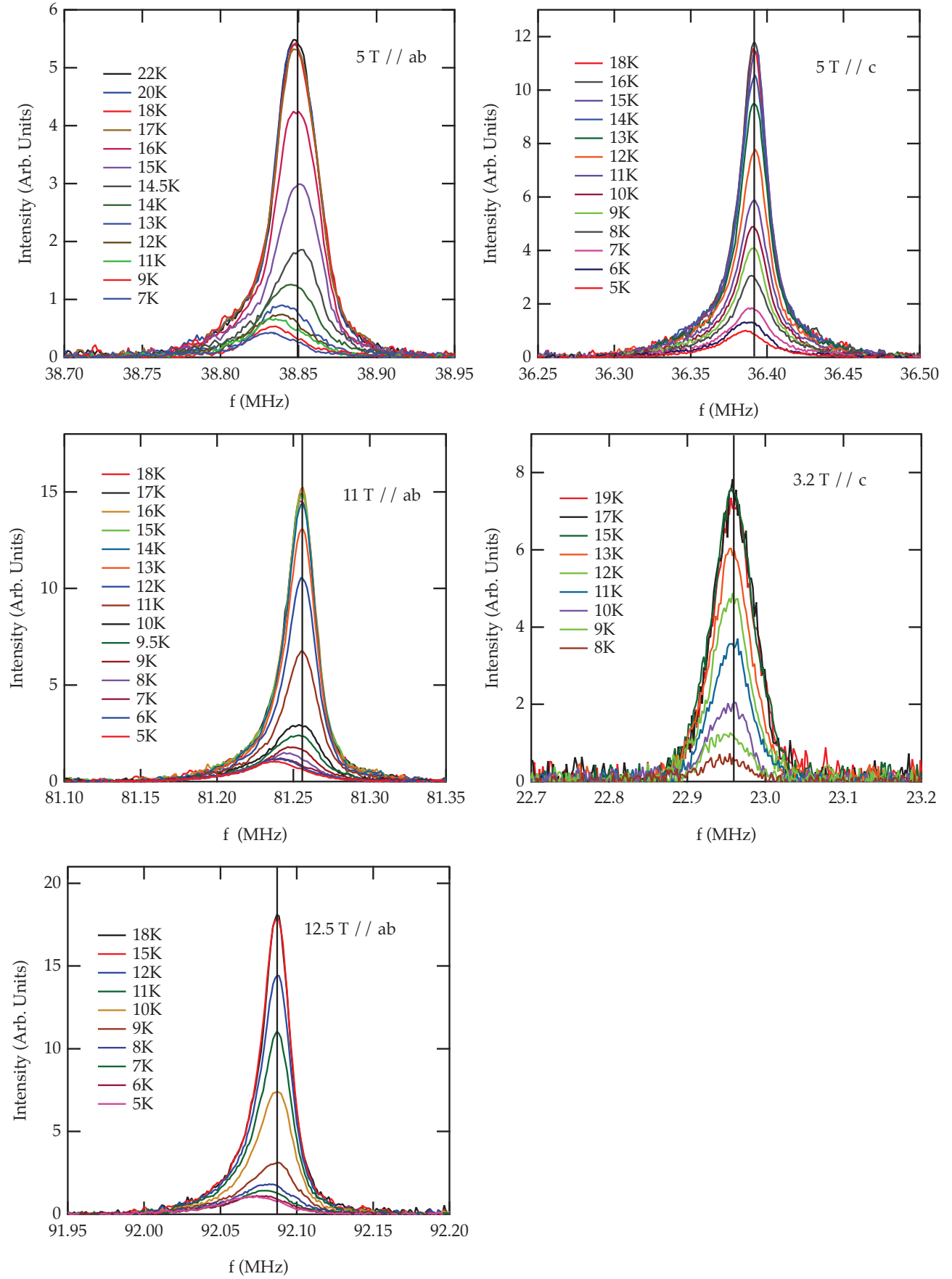


FIG. 5: Supplemental figure